

VERIFICATION OF TRANSLATION

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do hereby declare that I am well acquainted with the English and  
Japanese languages and I hereby certify that, to the best of my  
knowledge and belief, the following is a true and correct  
translation made by me into the English language of Japanese  
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[Title of the Invention] WHOLLY AROMATIC CONDENSATION POLYMER  
FIBER COMPOSITION

[Claims]

[Claim 1]

A wholly aromatic condensation polymer fiber composition comprising 100 parts by weight of a wholly aromatic condensation polymer and 0.01 to 100 parts by weight of carbon fibers having a diameter of 300 nm or less and an aspect ratio of 5.0 or more, the carbon fibers having an orientation coefficient F of 0.05 or more as expressed by the following formula (1):

[Equation 1]

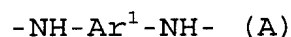
$$\begin{aligned} \langle \cos^2 \phi \rangle &= \frac{\int_0^{\pi/2} I(\phi) \cos^2 \phi \sin \phi d\phi}{\int_0^{\pi/2} I(\phi) \sin \phi d\phi} \\ F &= \frac{3 \langle \cos^2 \phi \rangle - 1}{2} \end{aligned} \quad (1)$$

wherein  $\phi$  represents the azimuth in X-ray diffraction measurement, and I represents the 002 diffraction intensity.

[Claim 2]

A fiber composition according to claim 1, wherein the wholly aromatic condensation polymer is the following general formulae (A) and (B):

[Chemical Formula 1]



-OC-Ar<sup>2</sup>-CO- (B) ,

wherein Ar<sup>1</sup> and Ar<sup>2</sup> each independently represent a C<sub>6-20</sub> divalent aromatic group.

[Claim 3]

A fiber composition according to claim 1 or 2, wherein the carbon fibers are pre-dispersed by physical treatment using a ball mill, a bead mill, or the like, so that the carbon fibers in the resulting fiber composition have an improved orientation coefficient F of 0.2 or more.

[Claim 4]

A fiber composition according to any one of claims 1 to 3, wherein the orientation coefficient F of the carbon fibers in the composition is improved by 0.01 or more by drawing during a spinning process.

[Claim 5]

A fiber composition according to any one of claims 1 to 4, wherein the orientation coefficient F after drawing is 0.1 or more.

[Claim 6]

A fiber composition according to any one of claims 1 to 5, wherein the amount of the carbon fibers is 0.1 to 60 parts by weight per 100 parts by weight of the wholly aromatic condensation polymer.

[Claim 7]

A fiber composition according to any one of claims 2 to

6, wherein, in the formula (A), Ar<sup>1</sup> is a paraphenylene group or a 3,4'-diphenylene ether group, and Ar<sup>2</sup> is a paraphenylene group.

[Claim 8]

A fiber composition according to any one of claims 2 to 7, wherein Ar<sup>1</sup> in the formula (A) is a paraphenylene group and a 3,4'-diphenylene ether group, the ratio therebetween being 1:0.8 to 1:1.2.

[Claim 9]

A fiber composition according to any one of claims 1 to 8, wherein the carbon fibers are carbon nanotubes.

[Claim 10]

A molded article comprising a fiber composition according to any one of claims 1 to 9.

[Claim 11]

A molded article according to claim 10, wherein the molded article is a fiber.

[Claim 12]

A molded article according to claim 10, wherein the molded article is a film.

[Detailed Description of the Invention]

[0001]

[Technical Field to which the Invention Belongs]

The present invention relates to a fiber composition comprising a wholly aromatic condensation polymer and carbon

fibers and having excellent mechanical properties due to the carbon fibers in the fiber composition being oriented in the direction of the orientation axis, and also to a molded article having excellent elasticity obtained therefrom.

[0002]

[Prior Art]

Wholly aromatic condensation polymer fiber compositions have a structure in which rigid aromatic rings are linked together. They have been widely applied as materials having excellent heat resistance, mechanical properties, and chemical resistance, in the form of fibers or films for electrically insulating materials, various reinforcing agents, bulletproof fibers, etc. Although this is one of the materials that are industrially extremely valuable, depending on the intended use, more advanced characteristics have been required for the resin.

[0003]

As one of the techniques that satisfy such required characteristics, attention has been recently focused on compositions comprising carbon fibers dispersed in a thermoplastic resin on a nanoscale, so-called nanocomposites. It has been disclosed that carbon fibers are oriented in a matrix by, for example, electrolysis, an appropriate shearing action, or combing (see, e.g., Patent Document 1.).

[0004]

[Patent Document 1] JP-B-8-26164 (pp. 5-7, FIG. 1)

[0005]

[Problems that the Invention is to Solve]

An object of the invention is to provide a wholly aromatic condensation polymer fiber composition especially having an improved elastic modulus, and a molded article having excellent elasticity obtained therefrom.

[0006]

[Means for Solving the Problems]

The invention is a wholly aromatic condensation polymer fiber composition comprising 100 parts by weight of a wholly aromatic condensation polymer and 0.01 to 100 parts by weight of carbon fibers having a diameter of 300 nm or less and an aspect ratio of 5.0 or more, the carbon fibers having an orientation coefficient  $F$  of 0.05 or more as expressed by the following formula (1).

[0007]

[Equation 2]

$$\begin{aligned} \langle \cos^2 \phi \rangle &= \frac{\int_0^{\pi/2} I(\phi) \cos^2 \phi \sin \phi d\phi}{\int_0^{\pi/2} I(\phi) \sin \phi d\phi} \\ F &= \frac{3 \langle \cos^2 \phi \rangle - 1}{2} \end{aligned} \quad (1)$$

[0008]

In the equation,  $\phi$  represents the azimuth in X-ray diffraction measurement, and  $I$  represents the 002 diffraction



intensity.

[0009]

The invention is also a molded article comprising the above wholly aromatic condensation polymer fiber composition, and more preferably a stretch-oriented film.

[0010]

[Mode for Carrying Out the Invention]

(Wholly Aromatic Condensation Polymer)

The wholly aromatic condensation polymer of the invention is a rigid linear molecule, in which the constitutional unit in the molecular chain is mainly an aromatic ring. Examples thereof include wholly aromatic polyamides, wholly aromatic polyesters, wholly aromatic polyimides, polybenzoxazole, polybenzimidazole, polybenzothiazole, polypyridobisimidazole, etc. Among these, wholly aromatic polyamides are preferable.

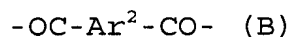
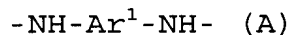
[0011]

(Wholly Aromatic Polyamide)

The wholly aromatic polyamide of the invention is a wholly aromatic polyamide consisting essentially of the following constitutional units.

[0012]

[Chemical Formula 2]



In the above general formulae (A) and (B),  $\text{Ar}^1$  and  $\text{Ar}^2$  each independently represent a  $\text{C}_{6-20}$  divalent aromatic group.

The constitutional units each preferably have a molar number that satisfies the following equation (3):

$$0.9 \leq a/b \leq 1.1 \quad (3),$$

wherein a represents the molar number of the repeating unit (A) of aromatic diamine, and b represents the molar number of the repeating unit (B) of aromatic dicarboxylic acid. The inherent viscosity  $\eta_{\text{inh}}$  thereof when dissolved in 98 wt% concentrated sulfuric acid to a concentration of 0.5 g/100 ml and measured at 30°C is preferably 0.05 to 20 (dl/g).

[0013]

In the above general formulae (A) and (B),  $\text{Ar}^1$  and  $\text{Ar}^2$  each independently represent a  $\text{C}_{6-20}$  divalent aromatic group. Specific examples thereof include a metaphenylene group, a paraphenylene group, an orthophenylene group, an orthophenylene group, a 2,6-naphthylene group, a 2,7-naphthylene group, a 4,4'-isopropylidene diphenylene group, a 4,4'-biphenylene group, a 4,4'-diphenylene sulfide group, a 4,4'-diphenylene sulfone group, a 4,4'-diphenylene ketone group, a 4,4'-diphenylene ether group, a 3,4'-diphenylene ether group, a metaxylylene group, a paraxylylene group, an orthoxylylene group, etc.

[0014]

One or more of the hydrogen atoms of these aromatic groups

may be each independently substituted with a halogen group such as fluorine, chlorine, bromine, etc.; a C<sub>1-6</sub> alkyl group such as a methyl group, an ethyl group, a propyl group, a hexyl group, etc.; a C<sub>5-10</sub> cycloalkyl group such as a cyclopentyl group, a cyclohexyl group, etc.; or a C<sub>6-10</sub> aromatic group such as a phenyl group, etc. The constitutional unit of the formulae (A) and/or (B) may be a copolymer containing two or more kinds of aromatic groups.

[0015]

Among these, Ar<sup>1</sup> is preferably a metaphenylene group, a paraphenylene group, or a 3,4'-diphenylene ether group. A combination of a paraphenylene group or a paraphenylene group with a 3,4'-diphenylene ether group is still more preferable, and a combination at a ratio of 1:0.8 to 1:1.2 is further more preferable.

[0016]

Ar<sup>2</sup> is preferably a metaphenylene group or a paraphenylene group, and more preferably a paraphenylene group. Specific examples of suitable polymers include poly(metaphenylene isophthalamide), poly(paraphenylene terephthalamide), and copolymerized wholly aromatic polyamides containing these as main components.

[0017]

These wholly aromatic polyamides can be produced by solution polymerization, interfacial polymerization, melt

polymerization, or a like conventionally known method. The polymerization degree of the polymer is preferably such that the inherent viscosity  $\eta_{inh}$  when dissolved in 98 wt% concentrated sulfuric acid to a concentration of 0.5 g/100 ml and measured at 30°C is 0.05 to 20 (dl/g), and more preferably 1.0 to 10 (dl/g).

[0018]

(Carbon Fiber)

The carbon fibers used in the invention preferably have a diameter of 300 nm or less, more preferably 0.3 to 250 nm, and still more preferably 0.4 to 100 nm. Those having a diameter of 0.3 nm or less are practically difficult to produce, and those having a diameter of 300 nm or more are poorly effective in improving dynamic strength.

[0019]

With respect to a preferable aspect ratio, although there is no upper limit, the lower limit is preferably 5.0 or more, more preferably 10.0 or more, and still more preferably 50.0 or more.

[0020]

A carbon fiber has the shape of a cylindrically rolled graphene sheet. Such a cylinder may have a single wall or multiple walls, and a multiple-wall cylinder is preferable. Graphene sheets may also be stacked in a cup-like shape.

[0021]

These carbon fibers are produced by a conventionally known method. Examples thereof include, but are not limited to, a gas phase flow process, a catalyst-carrying gas phase flow process, a laser ablation process, a high-pressure carbon monoxide process, an arc discharge process, etc.

[0022]

The fiber composition of the invention preferably contains carbon fibers in an amount of 0.01 to 100 parts by weight, more preferably 0.1 to 60 parts by weight, and still more preferably 1 to 10 parts by weight, per 100 parts by weight a wholly aromatic condensation polymer. When carbon fibers are present in an amount less than 0.01 parts by weight, effects in improving dynamic strength are hardly observed, while an amount more than 100 parts by weight results in difficulty in molding.

[0023]

(Orientation and Orientation Method)

In the invention, carbon fibers in the wholly aromatic condensation polymer fiber composition are oriented in the same direction as the orientation direction of the fibers. As an index of the orientation degree, an orientation coefficient  $F$  expressed by the following equation (1) is used. (Kakumoto, Masao et al, "*Kobunshi X-sen Kaisetsu* (high polymer X-ray diffraction)", 1968, Maruzen).

[0024]

[Equation 3]

$$\begin{aligned} \langle \cos^2 \phi \rangle &= \frac{\int_0^{\pi/2} I(\phi) \cos^2 \phi \sin \phi d\phi}{\int_0^{\pi/2} I(\phi) \sin \phi d\phi} \\ F &= \frac{3 \langle \cos^2 \phi \rangle - 1}{2} \end{aligned} \quad (1)$$

[0025]

In the equation,  $\phi$  represents the azimuth in X-ray diffraction measurement, and I represents the 002 intensity.

[0026]

In the invention, the upper limit of the value of the orientation coefficient F of the carbon fibers is mathematically 1.0, and the lower limit thereof is 0.05 or more, preferably 0.1 or more, more preferably 0.2 or more, and still more preferably 0.3 or more.

[0027]

Examples of orientation methods therefor include, for example, those that disperse carbon fibers in a polymer dope dissolved in a wholly aromatic condensation polymer solvent, and then subject the dispersion to rubbing, casting, flow orientation, liquid crystal orientation, shear orientation, or draw orientation. A molding method using a polymer dope may be a wet process, a dry process, or a combination of a wet process and a dry process. In the production of the resin composition of the invention, it is further preferable to further subject the obtained fiber composition to draw

orientation to thereby increase the orientation coefficient of the carbon fibers. The degree of increase in the orientation coefficient is preferably 0.01 or more, more preferably 0.05, and still more preferably 0.1 or more.

[0028]

(Dispersion)

As a method for dispersing carbon fibers in a wholly aromatic condensation polymer solvent, any of known methods can be applied. However, in order to improve dispersibility and obtain a highly oriented resin composition, it is preferable that, for example, carbon fibers in a solvent be physically treated using a ball mill, a bead mill, or the like, ultrasonically treated, or strongly sheared, or that carbon fibers be pretreated with acid before adding to the solvent, or surface-treated with an organic substance. Physical treatment using a ball mill, a bead mill, or the like is especially preferable, and this can increase the orientation coefficient  $F$  of the carbon fibers in the resulting fiber composition to 0.2 or more.

[0029]

(Molded Article)

The composition comprising a wholly aromatic condensation polymer and carbon fibers obtained according to the invention is useful as a molded material for fibers, films, pulp, etc. For example, the wholly aromatic condensation

polymer may be dissolved in an amide solvent such as dimethyl acetamide, 1-methyl-2-pyrrolidone, etc., or in an acid such as sulfuric acid, phosphoric acid, etc., and dry- or wet-processed into fibers, films, fibrils, etc. Such a molded article may be monoaxially or biaxially drawn to improve the orientation of the polymer and carbon fibers, thereby improving the mechanical properties. A preferable orientation factor is 2 to 20, and preferably 3 to 40. A preferable draw orientation temperature is 100°C to 800°C, and preferably 200°C to 600°C.

[0030]

(Fiber/Film)

The drawing process during the production of fibers from the resin composition of the invention increases the orientation degree of the carbon in the fiber composition, whereby highly elastic fibers having a fiber orientation coefficient  $F$  increased by 0.01 or more can be obtained. Further, the drawing process increases the orientation degree of the carbon fibers in the fiber composition, whereby highly elastic filaments having an orientation coefficient  $F$  after drawing of 0.1 or more can be obtained.

[0031]

The drawing process during the production of a film from the resin composition of the invention increases the orientation degree of the carbon fibers in the fiber



composition, whereby a highly elastic drawn film having an orientation coefficient F after drawing of 0.1 or more can be obtained.

[0032]

[Advantage of the Invention]

The fiber composition comprising a wholly aromatic condensation polymer and carbon fibers obtained according to the invention have excellent mechanical properties, especially elasticity, due to the carbon fibers in the fiber composition being oriented in the direction of the orientation axis.

[0033]

[Examples]

Hereinafter, the present invention will be described in further detail with reference to the examples, but is not limited thereto.

[0034]

(1) X-ray diffraction measurement: An X-ray generator (Model RU-B, manufactured by Rigaku) was used to measure incident X-rays under the following conditions: target CuK $\alpha$  rays, voltage 45 kV, current 70 mA. The measured incident X-rays were converged and monochromatized with a multilayer mirror manufactured by Osmic, and the cross-section of a sample was measured by a vertical transmission method. The diffracted X-rays were detected using a 200 mm  $\times$  250 mm imaging

plate (manufactured by Fuji Film), and measurement was conducted at a camera length of 250 mm.

[0035]

(5) Mechanical properties: A tensile test was conducted using a Tensilon Universal Tester 1225A manufactured by Orientech to determine the elastic modulus.

[0036]

[Preparation of Polymer Dope]

To a thoroughly dried three-necked flask equipped with a stirrer were added, at ordinary pressure, 1717.38 parts by weight of N-methylpyrrolidone, 18.82 parts by weight of p-phenylenediamine, and 34.84 parts by weight of 3,4'-diaminophenyl ether. The components were dissolved under nitrogen, and 70.08 parts by weight of terephthalic dichloride was added while stirring. The mixture was finally reacted at 80°C for 60 minutes, and then 12.85 parts by weight of calcium hydroxide was added to effect a neutralization reaction. The obtained polymer dope was reprecipitated with water, and the thus precipitated polymer had an inherent viscosity of 3.5 (dl/g).

[0037]

[Example 1]

To 300 parts by weight of NMP (N-methyl-2-pyrrolidone) was added 4.680 parts by weight of carbon fibers manufactured by Showa Denko (VGCF). The mixture was processed with a 28

kHz supersonic wave for 1 hour. The NMP solution was added to 1500 parts by weight of an NMP dope of the polymer obtained above and stirred at 90°C for 1 hour to give a uniform polymer dope. Using a cap having five 0.3-mm-diameter holes, the thus-obtained polymer dope as maintained at 80°C was extruded into a 56°C coagulation bath that is a 30 wt% NMP aqueous solution. The distance between the cap surface and the coagulation bath surface was set at 10 mm. Spun fibers were washed with water at 50°C, and dried at 120°C to give filaments.

[0038]

[Example 2]

To 300 parts by weight of NMP (N-methyl-2-pyrrolidone) was added 4.680 parts by weight of carbon fibers manufactured by Showa Denko (VGCF). The mixture was processed at 2500 rpm for 1 hour using 0.8-mm-diameter zirconium beads using a bead mill manufactured by NETZSCH, MINIZETA (air). The NMP solution was added to 1500 parts by weight of an NMP dope of the polymer obtained above and stirred at 90°C for 1 hour to give a uniform polymer dope. The thus-obtained polymer dope was used for fiber spinning in the same manner as in Example 1.

[0039]

[Example 3]

The filaments obtained in Example 1 were drawn at a draw ratio of 10 on a 500°C hot plate to give drawn filaments.

[0040]

[Example 4]

The filaments obtained in Example 2 were drawn at a draw ratio of 10 on a 500°C hot plate to give drawn filaments.

[0041]

[Comparative Example 1]

The same procedures as in Example 1 were performed without using carbon fibers.

[0042]

[Comparative Example 2]

The filaments obtained in Comparative Example 1 were drawn at a draw ratio of 10 on a 500°C hot plate to give drawn filaments.

[0043]

The physical properties are shown in a table.

[0044]

[Table 1]

	Draw Ratio (times)	Orientation Coefficient F	Elastic Modulus (GPa)
Example 1	1	0.093	5.2
Example 2	1	0.24	5.1
Example 3	10	0.105	62.1
Example 4	10	0.31	65.2
Comp. Ex. 1	1	-	4.9
Comp. Ex. 2	10	-	60.0

[Designation of Document] Abstract

[Abstract]

[Problem] To provide a fiber composition comprising a wholly aromatic condensation polymer and carbon fibers and having excellent mechanical properties, and a molded article having excellent elasticity therefrom.

[Means of Resolution] A wholly aromatic condensation polymer fiber composition comprising 100 parts by weight of a wholly aromatic condensation polymer and 0.01 to 100 parts by weight of carbon fibers having a diameter of 100 nm or less and an aspect ratio of 5.0 or more, the carbon fibers having an orientation coefficient F of 0.05 or more as expressed by the following formula (1):

[Equation 1]

$$\begin{aligned} \langle \cos^2 \phi \rangle &= \frac{\int_0^{\pi/2} I(\phi) \cos^2 \phi \sin \phi d\phi}{\int_0^{\pi/2} I(\phi) \sin \phi d\phi} \\ F &= \frac{3 \langle \cos^2 \phi \rangle - 1}{2} \end{aligned} \quad (1)$$

wherein  $\phi$  represents the azimuth in X-ray diffraction measurement, and I represents the 002 diffraction intensity.

[Selected Figure] None